



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/EP97/04573 (22) International Filing Date: 15 August 1997 (15.08.97) (30) Priority Data: 96306534.7 9 September 1996 (09.09.96) EP (34) Countries for which the regional or international application was filed: GB et al. (71) Applicant (for AU BB CA GB GH IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). (71) Applicant (for all designated States except AU BB CA GB GH IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).		(72) Inventors: BINLEY, Gary, Norman; 15 Raven Drive, Barton Seagrave, Kettering, Northampton NN15 6SD (GB). BURMESTER, Sabina, Silvia, Hanel; 71 Woodlark Road, Cambridge CB3 0HT (US). CHIARANUSSATI, Nuj; 23/F Tower 2, Clovelly Court, 12 May Road, Hong-kong (CN). WINCH, Paul, Jonathan; 13457 Velp Avenue, Saumico, WI 54173 (US). WIX, Loyd; 93 Hayway, Rushden, Northamptonshire NN10 6AQ (GB). (74) Agent: KIRSCH, Susan, Edith; Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB). (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: FROZEN PRODUCT AND PROCESS FOR THE PREPARATION THEREOF (57) Abstract <p>A frozen aerated product having no added emulsifier and preferably no added stabiliser and having a fat content of from 6 to 18 % which satisfies the following conditions: (a) % DF > [2.29 * %F]; (b) % ML100 < 80 % - [5.93 * %F]; and (c) an air cell size distribution such that the mean air cell size is less than 40 µm with a standard deviation of 20 µm; wherein DF = destabilised fat, F = fat, ML100 = mass loss after 100 minutes.</p>		

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FROZEN PRODUCT & PROCESS FOR THE PREPARATION THEREOFTechnical Field of the Invention

5 The invention relates to a high quality frozen aerated product, particularly an ice cream product and the manufacture thereof, wherein the frozen aerated product requires no addition of emulsifiers.

10 Background to the Invention

Traditionally frozen aerated products such as ice cream products contain stabilisers and emulsifiers in order to provide the desired quality product. However, it is now preferred to provide such products without additives. To date products provided without added stabilisers and emulsifiers have been inferior in quality in that they are fast melting, have a low percentage of destabilised fat, and are unstable to heat shock and hence quickly become very icy. Furthermore, such products have a reduced creaminess perception.

Clearly it would be advantageous to be able to provide a product having no added emulsifiers, and preferably no added stabilisers or emulsifiers which nevertheless retains its high quality.

Frozen aerated products such as ice cream are usually produced by a continuous process comprising the following steps:

- a) homogenising of ingredients
- b) pasteurisation
- c) cooling
- d) freezing and aeration
- 35 e) extrusion
- f) (optional) deep freezing

Normally the homogenisation step takes place in a first vessel, followed by continuous pasteurisation followed by cooling. The mixture is then transferred to a freezer, for example a scraped surface heat exchanger where the product is frozen to a temperature of approximately -6°C followed by quiescent cooling in a hardening tunnel.

The applicants have surprisingly found that if the product is subjected to cooling and shearing in a screw extruder prior to extrusion and any optional deep freezing, a high quality product may be prepared even in the absence of emulsifiers and preferably also in the absence of stabilisers.

Screw extruders such as single screw and twin screw extruders are widely used in the chemical industry for example in the production of plastics. It has also been proposed to use single screw or twin screw extruders in the freezing of ice-cream, see for example EP 561 118 and EP 401 512.

EP 713 650 discloses a method for manufacturing frozen aerated products in which the composition to be frozen is mixed, aerated and cooled to a temperature equal or less than -8°C prior to extrusion in a single twin screw device.

However, to date it has not been recognised that such screw extruders can advantageously be used to prepare a high quality frozen aerated product having no added emulsifiers or stabilisers.

Disclosure of the Invention

Accordingly the invention provides a frozen aerated product comprising;

- 5
 (i) 6 to 18% fat
 (ii) 0% emulsifier
 (iii) 0 to 1.0% stabiliser
 which satisfies the following conditions:

- 10
 (a) $\% DF > [2.29 * \%F]$;
 (b) $\% ML100 < 80\% - [5.93 * \%F]$; and
 (c) An air cell size distribution such that the mean air cell size is less than 40 μM with a standard deviation of 20 μM ;
- 15

wherein DF = destabilised fat
 F = fat
 ML100 = mass loss after 100 minutes

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Preferably the product has from 0 to 0.5% stabiliser, more preferably from 0 to 0.25 % stabiliser, even more preferred from 0 to 0.15% stabiliser, most preferred 0% stabiliser. Products having no stabiliser preferably have an ice crystal distribution such that each ice crystal has less than 1.75 neighbouring crystals touching in a 2D plane;

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A convenient process for the preparation of the frozen aerated product according to the invention comprises subjecting the product to be frozen to shear forces and cooling in a screw extruder prior to extrusion and optional deep freezing.

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The screw extruder can be either a single or multiple screw extruder, preferably however a single or twin screw extruder is used.

Preferably the product is extruded at a temperature of from -10°C to -30°C, more preferably from -10°C to -25°C, most preferably -10°C to -15°C.

- 5 The screw extruder may be employed after the conventional freezing and aeration step within for example a scraped surface heat exchanger. Alternatively all steps prior to extrusion, including if desirable homogenisation and pasteurisation, may be conducted within the screw extruder as described in either EP 713 650 or our copending European patent application EPA 96302718.0
- 10

Frozen aerated products according to the invention have been shown to have an increased perception of fat, characterised by increases in creamy texture, thickness, smoothness, initial smoothness and reduction of ice crystal quantity in mouth and ice crystal size in mouth.

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The percentage destabilised fat was measured using a solvent extraction technique. 10g of ice cream was melted for 4 hours at ambient temperature before extraction with petroleum solvent. The solvent was evaporated and the extracted destabilised fat was weighed, this was expressed as a percent of the weight of the total fat in the ice cream.

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The percentage mass loss after 100 minutes was determined by measuring the weight of melted ice cream every minute over the required time period.

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The air cell distribution and ice crystal distribution were determined using low temperature scanning electron microscopy (SEM).

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The mean air cell size measured for the products of the invention is thought to be important for providing products having a creamy texture. Conventionally prepared ice cream,

which is stabilised and emulsified will have a mean air cell size of from 60 to 100µm.

5 Preferably the frozen aerated product of the invention is a milk or fruit based frozen aerated confection such as ice cream, frozen yoghurt, sherbet, sorbet, and frozen custard.

10 Suitable ingredients and their preferred levels for such a frozen aerated confection are for example: Ice cream/custard: milk fat 6-18 wt%, milk solids non fat 2 to 15 wt%, sugar or other sweeteners 0.01 to 35 wt%, flavours 0-5 wt%, water 30 to 85 %wt.

15 Any stabiliser used in ice cream is suitable, for example Locust Bean Gum (LBG), Carrageenan, Guar gum, gelatin, CMC (Carboxy methyl cellulose) gum, pectin, algin products, and mixtures thereof.

ExamplesExample 1

5 An ice cream mixture having the following formulation:

12% Fat

12% Skimmed Milk Powder

15% Sucrose

61% Water

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was prepared in the conventional way and initially frozen in a standard ice cream freezer (scraped surface heat exchanger, SSHE) to a temperature of -6°C . Air was added to the mix in a ratio of 1:1.

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The outlet of the SSHE was connected by pipework to a single screw extruder with a refrigerated jacket which continued to freeze the ice cream to a temperature of $< -10^{\circ}\text{C}$. The single screw extruder had the following

20

geometry:

Barrel length 0.75m

Barrel diameter 0.2m

Screw pitch 0.135m (2 start)

Screw Channel depth 15 mm

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The single screw extruder was controlled to maintain a constant inlet pressure of 7 barg and a constant torque on the screw of 1500 Nm. The outlet pressure was 8 barg.

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An ice cream product was obtained which was emulsifier and stabiliser free having 28 % destabilised fat, 8.5% mass loss after 100 minutes, and the mean air cell size was $37\mu\text{M}$. Each ice crystal had less than 1.5 neighbouring crystals touching in a 2D plane.

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Furthermore, the ice-cream was of high quality having an excellent creamy texture and smoothness.

Example 2

An ice cream mixture having the following formulation:

5	<u>Ingredient</u>	<u>g/w/w</u>
	Butteroil	8.00
	Skimmed Milk Powder	10.00
	Sugars	19.58
	Stabiliser	0.16
10	Flavour	0.01
	Water	to 100

was prepared in the conventional way and initially frozen
in a standard ice cream freezer (scraped surface heat
exchanger, SSHE) to a temperature of -6°C . Air was added to
the mix in a ratio of 1:1.

The outlet of the SSHE was connected by pipework to a
single screw extruder with a refrigerated jacket which
continued to freeze the ice cream to a temperature of
 $< -10^{\circ}\text{C}$. The single screw extruder had the following
geometry:

	Barrel length	0.75m
	Barrel diameter	0.2m
25	Screw pitch	0.135m (2 start)
	Screw Channel depth	15 mm

The single screw extruder was controlled to maintain a
constant inlet pressure of 6 barg and a constant outlet
pressure of 4.5 barg. The flow rate was 225 L/hr, and the
torque on the screw was 1800Nm.

An ice cream product was obtained which was emulsifier
free having 23 % destabilised fat, 22% mass loss after 100
minutes, and the mean air cell size was $35\mu\text{M}$.

Furthermore, the ice-cream was of high quality having an

excellent creamy texture and smoothness. The quality of the ice cream was comparable to a conventional product containing 0.3% of emulsifier (a mono/di glyceride blend).

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Table

Table 1

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CLAIMS

1. A frozen aerated product comprising:

- 5 (i) 6 to 18% Fat;
(ii) 0% Emulsifier
(iii) 0 to 1.0% Stabiliser

which satisfies the following conditions:

10

- (a) $\% DF > [2.29 * \%F]$;
(b) $\% ML100 < 80\% - [5.93 * \%F]$; and
(c) An air cell size distribution such that the mean
air cell size is less than 40 μM with a standard
deviation of 20 μM ;

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wherein DF = destabilised fat
F = fat
ML100 = mass loss after 100 minutes

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2. A frozen aerated product according to claim 1 wherein
the product comprises from 0 to 0.5%, preferably 0 to
0.25% most preferably from 0 to 0.15% stabiliser.

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3. A frozen aerated product according to claim 1 or claim
2 wherein the product comprises 0% stabiliser.

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4. A process for the preparation of a frozen aerated
product according to any preceding claim wherein the
product to be frozen is subjected to shear forces and
cooling in a screw extruder prior to extrusion and
optional deep freezing.

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5. A process according to Claim 4 wherein the product to
be frozen is initially cooled to approximately -6°C in
a freezer before transferring into the screw extruder.

6. A process according to Claim 5 wherein the freezer is a scraped surface heat exchanger.
- 5 7. A process for the preparation of a frozen aerated product according to Claim 1, 2 or 3 comprising the steps of
- (a) homogenising of ingredients;
 - (b) pasteurisation;
 - (c) cooling;
 - 10 (d) freezing and aeration;
 - (e) extrusion; and
 - (f) (optional) deep freezing;
- 15 wherein steps (a) to (d) are conducted in a screw extruder.
8. A process according to any one of claims 4 to 7 wherein the screw extruder is a single screw extruder.
- 20 9. A process according to any one of claims 4 to 7 wherein the screw extruder is a twin screw extruder.
- 25 10. A process according to any one of Claims 4 to 7 wherein the product is extruded at a temperature of from -10°C to -30°C, preferably -10°C to -25°C, most preferably -10°C to -15°C.



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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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B. FIELDS SEARCHED

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IPC 6 A23G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 019 187 A (UNILEVER) 31 October 1979 see page 1, line 16 - line 30 see page 1, line 53 - line 55 ---	1-5, 10
A	GB 979 468 A (N. GAIETY) 16 July 1963 see the whole document ---	1
A	GB 948 456 A (N. GAIETY) 5 February 1964 see the whole document ---	1
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	<p>EP 0 561 118 A (E. WINDHAB ET AL.) 22 September 1993 see the whole document</p> <p> 11-12-13 A 11-12-13 B 14-15-16 A 14-15-16 B 17-18-19 A 17-18-19 B 20-21-22 A 20-21-22 B 23-24-25 A 23-24-25 B 26-27-28 A 26-27-28 B 29-30-31 A 29-30-31 B 32-33-34 A 32-33-34 B 35-36-37 A 35-36-37 B 38-39-40 A 38-39-40 B 41-42-43 A 41-42-43 B 44-45-46 A 44-45-46 B 47-48-49 A 47-48-49 B 50-51-52 A 50-51-52 B 53-54-55 A 53-54-55 B 56-57-58 A 56-57-58 B 59-60-61 A 59-60-61 B 62-63-64 A 62-63-64 B 65-66-67 A 65-66-67 B 68-69-70 A 68-69-70 B 71-72-73 A 71-72-73 B 74-75-76 A 74-75-76 B 77-78-79 A 77-78-79 B 80-81-82 A 80-81-82 B 83-84-85 A 83-84-85 B 86-87-88 A 86-87-88 B 89-90-91 A 89-90-91 B 92-93-94 A 92-93-94 B 95-96-97 A 95-96-97 B 98-99-100 A 98-99-100 B 101-102-103 A 101-102-103 B 104-105-106 A 104-105-106 B 107-108-109 A 107-108-109 B 110-111-112 A 110-111-112 B 113-114-115 A 113-114-115 B 116-117-118 A 116-117-118 B 119-120-121 A 119-120-121 B 122-123-124 A 122-123-124 B 125-126-127 A 125-126-127 B 128-129-130 A 128-129-130 B 131-132-133 A 131-132-133 B 134-135-136 A 134-135-136 B 137-138-139 A 137-138-139 B 140-141-142 A 140-141-142 B 143-144-145 A 143-144-145 B 146-147-148 A 146-147-148 B 149-150-151 A 149-150-151 B 152-153-154 A 152-153-154 B 155-156-157 A 155-156-157 B 158-159-160 A 158-159-160 B 161-162-163 A 161-162-163 B 164-165-166 A 164-165-166 B 167-168-169 A 167-168-169 B 170-171-172 A 170-171-172 B 173-174-175 A 173-174-175 B 176-177-178 A 176-177-178 B 179-180-181 A 179-180-181 B 182-183-184 A 182-183-184 B 185-186-187 A 185-186-187 B 188-189-190 A 188-189-190 B 191-192-193 A 191-192-193 B 194-195-196 A 194-195-196 B 197-198-199 A 197-198-199 B 200-201-202 A 200-201-202 B 203-204-205 A 203-204-205 B 206-207-208 A 206-207-208 B 209-210-211 A 209-210-211 B 212-213-214 A 212-213-214 B 215-216-217 A 215-216-217 B 218-219-220 A 218-219-220 B 221-222-223 A 221-222-223 B 224-225-226 A 224-225-226 B 227-228-229 A 227-228-229 B 230-231-232 A 230-231-232 B 233-234-235 A 233-234-235 B 236-237-238 A 236-237-238 B 239-240-241 A 239-240-241 B 242-243-244 A 242-243-244 B 245-246-247 A 245-246-247 B 248-249-250 A 248-249-250 B 251-252-253 A 251-252-253 B 254-255-256 A 254-255-256 B 257-258-259 A 257-258-259 B 260-261-262 A 260-261-262 B 263-264-265 A 263-264-265 B 266-267-268 A 266-267-268 B 269-270-271 A 269-270-271 B 272-273-274 A 272-273-274 B 275-276-277 A 275-276-277 B 278-279-280 A 278-279-280 B 281-282-283 A 281-282-283 B 284-285-286 A 284-285-286 B 287-288-289 A 287-288-289 B 290-291-292 A 290-291-292 B 293-294-295 A 293-294-295 B 296-297-298 A 296-297-298 B 299-300-301 A 299-300-301 B 302-303-304 A 302-303-304 B 305-306-307 A 305-306-307 B 308-309-310 A 308-309-310 B 311-312-313 A 311-312-313 B 314-315-316 A 314-315-316 B 317-318-319 A 317-318-319 B 320-321-322 A 320-321-322 B 323-324-325 A 323-324-325 B 326-327-328 A 326-327-328 B 329-330-331 A 329-330-331 B 332-333-334 A 332-333-334 B 335-336-337 A 335-336-337 B 338-339-340 A 338-339-340 B 341-342-343 A 341-342-343 B 344-345-346 A 344-345-346 B 347-348-349 A 347-348-349 B 350-351-352 A 350-351-352 B 353-354-355 A 353-354-355 B 356-357-358 A 356-357-358 B 359-360-361 A 359-360-361 B 362-363-364 A 362-363-364 B 365-366-367 A 365-366-367 B 368-369-370 A 368-369-370 B 371-372-373 A 371-372-373 B 374-375-376 A 374-375-376 B 377-378-379 A 377-378-379 B 380-381-382 A 380-381-382 B 383-384-385 A 383-384-385 B 386-387-388 A 386-387-388 B 389-390-391 A 389-390-391 B 392-393-394 A 392-393-394 B 395-396-397 A 395-396-397 B 398-399-400 A 398-399-400 B 401-402-403 A 401-402-403 B 404-405-406 A 404-405-406 B 407-408-409 A 407-408-409 B 410-411-412 A 410-411-412 B 413-414-415 A 413-414-415 B 416-417-418 A 416-417-418 B 419-420-421 A 419-420-421 B 422-423-424 A 422-423-424 B 425-426-427 A 425-426-427 B 428-429-430 A 428-429-430 B 431-432-433 A 431-432-433 B 434-435-436 A 434-435-436 B 437-438-439 A 437-438-439 B 440-441-442 A 440-441-442 B 443-444-445 A 443-444-445 B 446-447-448 A 446-447-448 B 449-450-451 A 449-450-451 B 452-453-454 A 452-453-454 B 455-456-457 A 455-456-457 B 458-459-460 A 458-459-460 B 461-462-463 A 461-462-463 B 464-465-466 A 464-465-466 B 467-468-469 A 467-468-469 B 470-471-472 A 470-471-472 B 473-474-475 A 473-474-475 B 476-477-478 A 476-477-478 B 479-480-481 A 479-480-481 B 482-483-484 A 482-483-484 B 485-486-487 A 485-486-487 B 488-489-490 A 488-489-490 B 491-492-493 A 491-492-493 B 494-495-496 A 494-495-496 B 497-498-499 A 497-498-499 B 500-501-502 A 500-501-502 B 503-504-505 A 503-504-505 B 506-507-508 A 506-507-508 B 509-510-511 A 509-510-511 B 512-513-514 A 512-513-514 B 515-516-517 A 515-516-517 B 518-519-520 A 518-519-520 B 521-522-523 A 521-522-523 B 524-525-526 A 524-525-526 B 527-528-529 A 527-528-529 B 530-531-532 A 530-531-532 B 533-534-535 A 533-534-535 B 536-537-538 A 536-537-538 B 539-540-541 A 539-540-541 B 542-543-544 A 542-543-544 B 545-546-547 A 545-546-547 B 548-549-550 A 548-549-550 B 551-552-553 A 551-552-553 B 554-555-556 A 554-555-556 B 557-558-559 A 557-558-559 B 560-561-562 A 560-561-562 B 563-564-565 A 563-564-565 B 566-567-568 A 566-567-568 B 569-570-571 A 569-570-571 B 572-573-574 A 572-573-574 B 575-576-577 A 575-576-577 B 578-579-580 A 578-579-580 B 581-582-583 A 581-582-583 B 584-585-586 A 584-585-586 B 587-588-589 A 587-588-589 B 590-591-592 A 590-591-592 B 593-594-595 A 593-594-595 B 596-597-598 A 596-597-598 B 599-600-601 A 599-600-601 B 602-603-604 A 602-603-604 B 605-606-607 A 605-606-607 B 608-609-610 A 608-609-610 B 611-612-613 A 611-612-613 B 614-615-616 A 614-615-616 B 617-618-619 A 617-618-619 B 620-621-622 A 620-621-622 B 623-624-625 A 623-624-625 B 626-627-628 A 626-627-628 B 629-630-631 A 629-630-631 B 632-633-634 A 632-633-634 B 635-636-637 A 635-636-637 B 638-639-640 A 638-639-640 B 641-642-643 A 641-642-643 B 644-645-646 A 644-645-646 B 647-648-649 A 647-648-649 B 650-651-652 A 650-651-652 B 653-654-655 A 653-654-655 B 656-657-658 A 656-657-658 B 659-660-661 A 659-660-661 B 662-663-664 A 662-663-664 B 665-666-667 A 665-666-667 B 668-669-670 A 668-669-670 B 671-672-673 A 671-672-673 B 674-675-676 A 674-675-676 B 677-678-679 A 677-678-679 B 680-681-682 A 680-681-682 B 683-684-685 A 683-684-685 B 686-687-688 A 686-687-688 B 689-690-691 A 689-690-691 B 692-693-694 A 692-693-694 B 695-696-697 A 695-696-697 B 698-699-700 A 698-699-700 B 701-702-703 A 701-702-703 B 704-705-706 A 704-705-706 B 707-708-709 A 707-708-709 B 710-711-712 A 710-711-712 B 713-714-715 A 713-714-715 B 716-717-718 A 716-717-718 B 719-720-721 A 719-720-721 B 722-723-724 A 722-723-724 B 725-726-727 A 725-726-727 B 728-729-730 A 728-729-730 B 731-732-733 A 731-732-733 B 734-735-736 A 734-735-736 B 737-738-739 A 737-738-739 B 740-741-742 A 740-741-742 B 743-744-745 A 743-744-745 B 746-747-748 A 746-747-748 B 749-750-751 A 749-750-751 B 752-753-754 A 752-753-754 B 755-756-757 A 755-756-757 B 758-759-760 A 758-759-760 B 761-762-763 A 761-762-763 B 764-765-766 A 764-765-766 B 767-768-769 A 767-768-769 B 770-771-772 A 770-771-772 B 773-774-775 A 773-774-775 B 776-777-778 A 776-777-778 B 779-780-781 A 779-780-781 B 782-783-784 A 782-783-784 B 785-786-787 A 785-786-787 B 788-789-790 A 788-789-790 B 791-792-793 A 791-792-793 B 794-795-796 A 794-795-796 B 797-798-799 A 797-798-799 B 800-801-802 A 800-801-802 B 803-804-805 A 803-804-805 B 806-807-808 A 806-807-808 B 809-810-811 A 809-810-811 B 812-813-814 A 812-813-814 B 815-816-817 A 815-816-817 B 818-819-820 A 818-819-820 B 821-822-823 A 821-822-823 B 824-825-826 A 824-825-826 B 827-828-829 A 827-828-829 B 830-831-832 A 830-831-832 B 833-834-835 A 833-834-835 B 836-837-838 A 836-837-838 B 839-840-841 A 839-840-841 B 842-843-844 A 842-843-844 B 845-846-847 A 845-846-847 B 848-849-850 A 848-849-850 B 851-852-853 A 851-852-853 B 854-855-856 A 854-855-856 B 857-858-859 A 857-858-859 B 860-861-862 A 860-861-862 B 863-864-865 A 863-864-865 B 866-867-868 A 866-867-868 B 869-870-871 A 869-870-871 B 872-873-874 A 872-873-874 B 875-876-877 A 875-876-877 B 878-879-880 A 878-879-880 B 881-882-883 A 881-882-883 B 884-885-886 A 884-885-886 B 887-888-889 A 887-888-889 B 890-891-892 A 890-891-892 B 893-894-895 A 893-894-895 B 896-897-898 A 896-897-898 B 899-900-901 A 899-900-901 B 902-903-904 A 902-903-904 B 905-906-907 A 905-906-907 B 908-909-910 A 908-909-910 B 911-912-913 A 911-912-913 B 914-915-916 A 914-915-916 B 917-918-919 A 917-918-919 B 920-921-922 A 920-921-922 B 923-924-925 A 923-924-925 B 926-927-928 A 926-927-928 B 929-930-931 A 929-930-931 B 932-933-934 A 932-933-934 B 935-936-937 A 935-936-937 B 938-939-940 A 938-939-940 B 941-942-943 A 941-942-943 B 944-945-946 A 944-945-946 B 947-948-949 A 947-948-949 B 950-951-952 A 950-951-952 B 953-954-955 A 953-954-955 B 956-957-958 A 956-957-958 B 959-960-961 A 959-960-961 B 962-963-964 A 962-963-964 B 965-966-967 A 965-966-967 B 968-969-970 A 968-969-970 B 971-972-973 A 971-972-973 B 974-975-976 A 974-975-976 B 977-978-979 A 977-978-979 B 980-981-982 A 980-981-982 B 983-984-985 A 983-984-985 B 986-987-988 A 986-987-988 B 989-990-991 A 989-990-991 B 992-993-994 A 992-993-994 B 995-996-997 A 995-996-997 B 998-999-1000 A 998-999-1000 B </p>	1,4-6, 8-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat Application No

PCT/EP 97/04573

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2019187 A	31-10-79	AT 375817 B AU 4640979 A BE 875826 A CA 1117355 A CH 652567 A DE 2916395 A DK 166879 A FR 2423986 A LU 81186 A NL 7903236 A SE 7903559 A US 4219581 A ZA 7901935 A	10-09-84 01-11-79 24-10-79 02-02-82 29-11-85 31-10-79 25-10-79 23-11-79 07-11-79 26-10-79 25-10-79 26-08-80 26-11-80
GB 979468 A		NONE	
GB 948456 A		NONE	
EP 559316 A	08-09-93	JP 5328905 A CA 2087648 A DE 559316 T US 5403611 A	14-12-93 23-07-93 24-02-94 04-04-95
EP 351476 A	24-01-90	AU 603693 B AU 2100088 A US 5024066 A	22-11-90 22-02-90 18-06-91
DE 2538858 A	10-03-77	NONE	
WO 9739637 A	30-10-97	AU 2509097 A	12-11-97
GB 1439143 A	09-06-76	AT 335831 B AU 5664173 A BE 800802 A CA 1028890 A DE 2329816 A FR 2187234 A JP 1162650 C JP 49132264 A JP 57049180 B	12-04-77 12-12-74 12-12-73 04-04-78 10-01-74 18-01-74 10-08-83 18-12-74 20-10-82

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat Application No

PCT/EP 97/04573

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1439143 A	14-12-73	NL 7308106 A, B,	14-12-73
WO 9211769 A	23-07-92	US 5112626 A	12-05-92
		US 5175013 A	29-12-92
		AU 653770 B	13-10-94
		AU 9148791 A	17-08-92
		CA 2099243 A, C	01-07-92
		DE 69108569 D	04-05-95
		DE 69108569 T	03-08-95
		EP 0565596 A	20-10-93
		JP 6506825 T	04-08-94
EP 713650 A	29-05-96	AU 3770095 A	30-05-96
		CA 2163284 A	24-05-96
		CN 1132595 A	09-10-96
		CZ 9503076 A	17-07-96
		FI 955594 A	24-05-96
		HU 74491 A	28-01-97
		JP 8205783 A	13-08-96
		NO 954687 A	24-05-96
		PL 311434 A	27-05-96
		SG 35034 A	01-02-97
		SK 144495 A	05-06-96
EP 401512 A	12-12-90	DE 3918268 C	26-07-90
		AT 116528 T	15-01-95
		AU 5670190 A	07-01-91
		WO 9014775 A	13-12-90
		ES 2066900 T	16-03-95
WO 9321777 A	11-11-93	AT 155650 T	15-08-97
		AU 667111 B	07-03-96
		AU 4265793 A	29-11-93
		CA 2134125 A	11-11-93
		CN 1079110 A	08-12-93
		DE 69312482 D	04-09-97
		DE 69312482 T	15-01-98
		EP 0637207 A	08-02-95
		FI 944988 A	24-10-94
		NO 944022 A	24-10-94

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/04573

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9321777 A		US 5486373 A	23-01-96
		ZA 9302842 A	24-10-94
EP 438201 A	24-07-91	NL 9000101 A	16-08-91
		DE 69101561 D	11-05-94
		DE 69101561 T	28-07-94
		JP 4218340 A	07-08-92
		US 5308628 A	03-05-94
EP 561118 A	22-09-93	DE 4202231 C	09-06-93
		US 5345781 A	13-09-94
		AT 158151 T	15-10-97